

CHARACTERIZATION OF POLYANILINE BASED POLYMER LIGHT-EMITTING DEVICES DURING OPERATION BY ELECTRICAL IMPEDANCE SPECTROSCOPY

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Abstract

Polyaniline was used as hole injection material for polymer light emitting devices (PLED) spin coated from a water based polyaniline/poly-styrenesulfonate (Pani/PSS) dispersion. Data presented here were based on red, yellow, green and blue light emitting polymers (LEP). Depending on the applied bias voltages the devices were studied by electrical impedance spectroscopy (EIS) in a wide frequency range. Experimental data could only be fitted by applying an equivalent circuit consisting of three RC elements in series. By separating the frequency dependent bulk and interface contributions, the bulk and junction resistance and capacitance were determined for various current densities. Variation in high interfacial capacitance was observed in the devices before and after stressing the PLEDs with a constant current of 10 mA/cm² for 100 h.

Keywords: PLED, polyaniline, hole injection layer, light-emitting polymers, impedance spectroscopy

1. Introduction

Polymeric light emitting diodes have emerged as one of the most promising technologies for inclusion in flat-panel displays. They have various advantages for high display quality such as light weight, wide viewing angle, bright emission and rapid response. However PLED device performance is still strongly required to be improved in power efficiency, long life-time and high color purity. Unfortunately, most light-emitting polymers still lack a satisfactory stability, especially the blue.

Impedance spectroscopic investigations on PPV-based LEDs are reported in the literature by several groups with different results and interpretations. Impedance spectra on ITO/PPV/Al devices were described by two semicircles within a Schottky model representing bulk and junction region [1,2] or by the presence of an interfacial oxide layer at the PPV/Al contact [3]. Equivalent circuits using three RC elements suggested a spatial variation of the conductivity in the PPV film [4]. A more complex equivalent circuit was proposed by analyzing the Poisson's and the hole and electron continuity equations [5].

Here we present a detailed study of PLEDs with different LEPs by electrical impedance spectroscopy in a wide frequency range as a function of current corresponding to the applied bias voltage. From the frequency dependence information on the transport parameters of the red, yellow, green and blue light-emitting materials and the equivalent circuit necessary to describe the device characteristics are expected. The current dependence should give information about changes in interfacial and bulk regions.

2. Experimental

The light-emitting devices were prepared by Covion by spin coating and curing a 80 nm layer of Pani/PSS as HIL onto indium tin oxide (ITO) patterned glass substrates followed by spin coating of the 80 nm light-emitting polymer layer. A water based Pani/PSS dispersion (Ormecon PAT020) with a conductance of 1×10^{-5} S/cm and a work function of 5.1 eV was used [6]. Light-emitting polymers were Red (AEF 2145), Yellow (PDY 132), Green (AEF 2394) and Blue (AEF 6053) from Covion Semiconductors GmbH [7]. As cathode material, 6 nm Ba with a capping layer of 100 nm Al for lowering cathode resistance was deposited by evaporation. Finally, the device is protected from water and oxygen using a glass lid. The average electrode area was 16 mm².

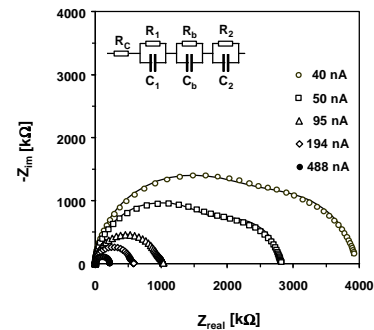
For electrical impedance spectroscopy and measurement of IV characteristics an Autolab potentiostat/galvanostat model PGSTAT 30 was used. For EIS a digital signal converter, a signal conditioning unit and a fast analog to digital converter with two channels (model Autolab FRA 2) was used in a frequency sweep range from 10 mHz to 1 MHz. An ac perturbation signal of 50 mV was applied upon constant different forward dc bias in the range of 0 to 5 V. During the measurements the devices were housed in a Faradaic cage. Impedance data were fitted to an equivalent circuit using simulation and modeling software based on the work of Boukamp [8]. All experiments were performed at room temperature.

The PLED devices were stressed at 10 mA/cm² applied by a Keithley source meter, model 2400.

3. Results and Discussion

In order to evaluate experimental data, an equivalent circuit consisting of three parallel RCs in a serial combination with a contact resistance R_c as shown in the inset of Fig. 1 was used. In the equivalent circuit the interfacial layers correspond to the junction resistance R_1 and R_2 and capacitance C_1 and C_2 . Between these depletion layers exists a bulk region represented by a resistor R_b and a capacitance C_b .

Fig. 1. Impedance Cole-Cole plots of unstressed Pani/Green/Ba



device at various currents showing experimental (symbols) and fitted (solid line) data. The left semicircles were assigned to the polymer bulk and the right semicircles to the depletion layers. For the devices a model was assumed where the Pani/LEP and the LEP/Ba interfaces were regarded as Schottky barriers. The contact of LEP with the high work function PAI was regarded as ohmic but the interaction of light-emitting polymer with the

Report Documentation Page				Form Approved OMB No. 0704-0188	
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1. REPORT DATE JUL 2004		2. REPORT TYPE N/A		3. DATES COVERED -	
4. TITLE AND SUBTITLE Characterization of Polyaniline Based Polymer Light-Emitting Devices During Operation by Electrical Impedance Spectroscopy				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) AOARD/AFOSR Unit 45002 APO AP 96337-5002				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release, distribution unlimited					
13. SUPPLEMENTARY NOTES Proceedings of the International Conference for the Science and Technology of Synthetic Metals (ICSM 2004). Held in New South Wales, Australia on Jun 28- July 2 2004. Copyrighted: Government Purpose Rights License. See also ADM001811					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UU	18. NUMBER OF PAGES 2	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			

conducting polymer can result in the creation of defect states forming an interfacial region between hole injection layer and the LEP [9]. Similar effects have been reported for hole injection from an Ag anode into a dialkoxy-PPV explained by electron trapping near the anode [10]. At the cathode doping [11], surface contamination [12] and different Fermi levels can be responsible for the formation of a Schottky contact at the interface LEP/metal [4]. Band bending at the interfaces are accompanied by an inhomogeneous electric field distribution and depletion layers occur at the interfaces. Between the Schottky barriers a space-charge region in the bulk is formed. It is also important that both electrodes inject carriers that can dominate the transport.

By fitting the impedance data the resistance R_b and the capacitance of the bulk material C_b and the interfacial resistance R_1 and R_2 and capacitance C_1 and C_2 were obtained. A contact resistance of about 30 Ω independent of applied bias voltage was approximately the same for all devices. The dependence of the capacitance on the current corresponding to the applied bias voltages is shown in Fig. 2. The capacities of the interfacial regions were significantly higher than the capacitance in the bulk. The sum of the resistance values R_c , R_b , R_1 and R_2 agreed very well with the numerical derivatives of the corresponding IV curves of the devices.

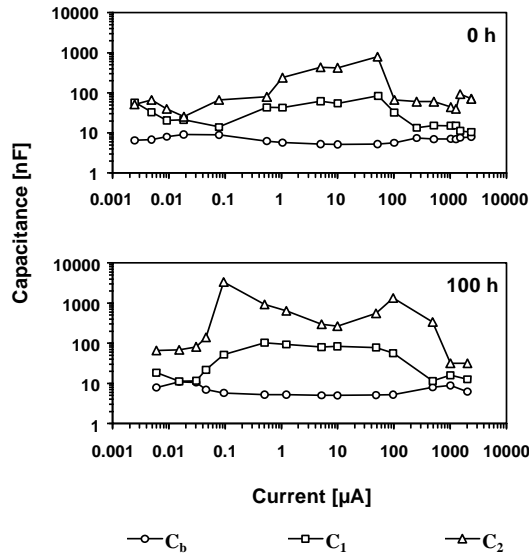


Fig. 2. Capacitance for bulk and interfacial regions for stressed and unstressed Pani/Yellow/Ba device as a function of current.

We believe that C_2 can be related to the depletion area at the PAni/LEP interface. The magnitude of the capacitance C_2 was much higher than the bulk capacitance and the capacitance C_1 that was related to the LEP/Ba interface. This was proven by variation of hole injection layer thickness. For a given device the values for C_2 changed proportional to hole injection layer thickness. When the cathode consisted of LiF/Al only changes in C_1 were obvious.

As shown in Fig. 2 for a yellow device the capacitance of C_b was almost independent of current density. For C_1 and C_2 an increase of capacity was observed for the unstressed and stressed devices. At higher current densities the capacitance decreased to the initial values forming a current range for high capacitance. For different LEPs these ranges are summarized in Table 1.

Table 1. Current range for high capacitance in interfacial regions for different light-emitting polymers before and after stressing the devices at 10 mA/cm².

operating time [h]	Current range [μ A] for LEP			
	Red	Yellow	Green	Blue
0	10 - 100	1 - 100	0.04 - 100	1 - ≥ 10000
100	10 - 500	0.05 - 1000	0.01 - 1000	0.01 - ≥ 10000

For red only a slight variation in capacitance was observed. For all other devices this broadening increased in the sequence yellow, green, blue.

4. Conclusions

Impedance data for PLEDs could only be fitted by applying an equivalent circuit consisting of three RC elements in series. By separating bulk and interface contributions, bulk and interfacial capacitance were identified and determined at various current densities. Current ranges with high capacitance were observed in devices based on yellow, green and blue light-emitting polymers. The highly capacitive junction provides interfacial electron-hole recombination, which can lower life-time and efficiency of the displays. It is important that the charge mobility is balanced in the devices in order to maximize power conversion efficiency and minimize degradation of the material by oxidation. As the range for high capacitance was broadest for the blue light-emitting material the unstable electroluminescence of this material can be better understood.

Acknowledgments

We wish to thank the team of Covion Semiconductors GmbH (Frankfurt, Germany) for preparing and providing the devices and their active collaboration and useful discussions.

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